

REPORT DOCUMENTATION PAGE**Form Approved**
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Service, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188) Washington, DC 20503.

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY) 23-11-2010		2. REPORT TYPE Final	3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Characterization, Modeling, and Accelerating Emulation of Aircraft Coating Exposure and Degradation.			5a. CONTRACT NUMBER FA9550-07-1-0370	
			5b. GRANT NUMBER	
			5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Bierwagen, Gordon			5d. PROJECT NUMBER	
			5e. TASK NUMBER	
			5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Coatings & Polymeric Materials North Dakota State University NDSU Dept. 2760 PO Box 6050 Fargo, ND 58108-6050			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR 875 N Randolph Suite 325 Arlington VA 22203			10. SPONSOR/MONITOR'S ACRONYM(S)	
			11. SPONSORING/MONITORING AGENCY REPORT NUMBER AFRL-OSR-VA-TR-2012-0040	
12. DISTRIBUTION AVAILABILITY STATEMENT Distribution A				
13. SUPPLEMENTARY NOTES				
14. ABSTRACT The Air Force stations its aircraft in many geographical locations worldwide, and some of these sites have specific exposure conditions and atmospheric chemistry that make them especially "potent" in their effects on aircraft coatings. In a period in which the Air Force is making the transition away from chromate-based corrosion protection for its air fleet, it is very important that the test methods used in qualifying new protective coatings and metal pretreatments properly reflect the stresses and conditions to which the aircraft are exposed. Further, these tests must be truly accelerated tests in that they MUST accurately reflect the stresses and hazards that the aircraft and its coatings systems will see during its lifetime. The present suite of tests now used in coating accelerated testing need to be upgraded to reflect the current state-of-the-art in environmental science concerning the exposure which the aircraft will really see, as well as the state-of-the-art in measurements and modeling of coating degradation and failure in the field and the laboratory. NDSU proposes to do an extensive review and update of the suite of tests now currently used to qualify coatings and coating systems for DoD aircraft. It will choose those tests, such as ASTM B117, that have obvious flaws, and develop or implement alternate test protocols that reflect the best current science and document these measurement as appropriate test methods, including the accelerating factors of the test, and the modeling of the test to make it predictive of future performance of the coatings. The coatings used in developing the improved methodologies will include both the existing chromate-based systems upon which all of the present tests and qualification procedures have been built (and biased as well), as well as all the best of the chromate replacement coatings such as the Mg-rich technology from NDSU.				

INSTRUCTIONS FOR COMPLETING SF 298

15. SUBJECT TERMS

NDSU, modeling, geographical, pretreatments, coatings, environmental, and Mg

16. SECURITY CLASSIFICATION OF:**17. LIMITATION OF
ABSTRACT****18. NUMBER
OF PAGES****19a. NAME OF RESPONSIBLE PERSON**

a. REPORT

b. ABSTRACT

c. THIS PAGE

19b. TELEPHONE NUMBER *(Include area code)*

Final Report to Air Force Office of Scientific Research

September 30, 2009

Re: Grant #: FA9550-07-1-0370

Program Manager: Major Michelle Ewy

Characterization, Modeling, and Accelerating Emulation of Aircraft Coating Exposure and Degradation.

Prepared by

Department of Coatings & Polymeric Materials

North Dakota State University

NDSU Dept. 2760

PO Box 6050

Fargo, ND 58108-6050

Prof. Gordon P. Bierwagen

Principal Investigator

Prof. Stuart Croll & Prof. Dennis Tallman,

Co-PI's

Project Team

Faculty	Graduate Students	Post Docs	Undergraduates
Gordon Bierwagen	Bobbi Jo Merten	Maocheng Yan	
Stuart Croll	Jun Nie	Jinhai Wang	
Dennis Tallman	Quan Su	Yechung Wang	
Kerry Allahar	Andrew Huovinen	Duhua Wang	
Brian Hinderliter	Dilhan Fernando		
Dante Battocchi			
	Hong Xu		
	Xiadong Shi		
	Tiantian Chen		

Abstract of Work Effort from Project Proposal:

The Air Force stations its aircraft in many geographical locations worldwide, and some of these sites have specific exposure conditions and atmospheric chemistry that make them especially “potent” in their effects on aircraft coatings. In a period in which the Air Force is making the transition away from chromate-based corrosion protection for its air fleet, it is very important that the test methods used in qualifying new protective coatings and metal pretreatments properly reflect the stresses and conditions to which the aircraft are exposed. Further, these tests must be truly accelerated tests in that they **MUST** accurately reflect the stresses and hazards that the aircraft and its coatings systems will see during its lifetime. The present suite of tests now used in coating accelerated testing need to be upgraded to reflect the current state-of-the-art in environmental science concerning the exposure which the aircraft will really see, as well as the state-of-the-art in measurements and modeling of coating degradation and failure in the field and the laboratory. NDSU proposes to do an extensive review and update of the suite of tests now currently used to qualify coatings and coating systems for DoD aircraft. It will choose those tests, such as ASTM B117, that have obvious flaws, and develop or implement alternate test protocols that reflect the best current science and document these measurement as appropriate test methods, including the accelerating factors of the test, and the modeling of the test to make it predictive of future performance of the coatings. The coatings used in developing the improved methodologies will include both the existing chromate-based systems upon which all of the present tests and qualification procedures have been built (and biased as well), as well as all the best of the chromate replacement coatings such as the Mg-rich technology from NDSU, the Deft/UMR materials and others as they are available. It will then attempt to recommend, based on its own work and the work of others the best suite of measurements and models for coating performance that exist or can be easily developed for the AF.

Below is an outline of this research program as taken from the original project proposal.

Characterization, Modeling, and Accelerating Emulation of Aircraft Coating Exposure and Degradation

1. Assessment of Exposure in Aircraft Coatings

1.1 Environmental Factors

1.2 Specific Studies on the Environmental Effects of Exposure to Moisture

1.3 Advanced Assessment of the Transport of Water in Organic Coatings

1.4 Characterization of the Performance of Mg-rich Primers in Exposure

2. Modeling of Exposure

2.1 Modeling of Exposure and its Effect on Coatings

2.2 Modeling of Water Transport in Organic Coatings

2.3 Modeling of Active Pigmented Coatings

3. Development of Test Methods

3.1 Mechanical strains, Voids, Cracks and Fatigue

3.2 Combinatorial Approaches to Coating Degradation

3.3 Consideration of New Corrosion Protection Test Method

3.4 Accelerated Testing by Enhanced Transport Processes

4. Initiating research topic

Ionic Liquids as Electrochemical Solvents for Coatings Characterization and Coatings Deposition on Metal Substrates

In addition to the work above, we included studies of Flexible Mg-rich Primers for Aircraft at the request of Mike Spicer of the AFRL/WPAFB Coating Technology Integration Office. This work is mainly contained in the MS Thesis of T. Chen, and was presented publicly on October 14, 2010 at the NACE Eastern Area Conference in Alexandria, VA.

The work presented in detail in this report is that work as yet unpublished that was performed under this grant. We will cite references to published work when there is no original unpublished work to be given. We identify below the published work from full or partial support by this Grant. Graduate student theses describing student research that was supported in full or in part will be cited as pertinent.

We also append the two annual reports on the contract as pertinent to summarizing the project effort and results of the research effort performed under this grant.

ANNUAL REPORT 1: Reporting Period: September 1, 2007 to July 31, 2008

Program Manager: Major Jennifer Gresham

The objectives of this program remain unchanged from the original statement of work.

Annual accomplishments:

GPBierwagen Group: Work was performed on the use of ionic liquids in emulating cyclic wet-dry exposure using ionic liquids. The acceleration of coating failure using low velocity laminar flow of electrolyte indicates an increase in failure rate without changing the mechanism of failure can be achieved. We have been expanding our studies of the AC-DC-AC test protocol for acceleration of coating failure in aircraft coating systems, and we used electrochemical noise methods/shot noise to determine the mechanism of corrosion failure under the accelerating conditions.

Stuart Croll Group: Finite difference calculations have been made of the diffusion of water into coatings in different weathering cycles. They demonstrate very clearly how accelerated testing protocols may concentrate water at different depths than may natural weathering. Thus coating failure due to adhesion loss or hydrolysis can be very different between accelerated testing protocols, depending on temperature level and cycle period, and will be different, in general, to failures experienced in the field. This provides clear insight into discrepancies between accelerated weathering tests in the laboratory and in field experience.

Dennis E. Tallman Group: This project deals with the thermal cycling and the wet/dry cycling of organic coatings employing ionic liquid media, research that was led by Research Assistant Professors Kerry Allabar and Brian Hinderliter. Some of the results are discussed above. The results of these studies are also discussed in detail in the publications cited below. Additionally, we have continued our studies of electron transfer at AA 2024-T3 using scanning electrochemical microscopy. We have characterized the types of intermetallic particles that dominate the electron transfer process and have found correlations with the surface conductivity of these particles as measured by conducting atomic force microscopy. We have written a LabView based program that interactively fits theory to experimentally measured probe approach curves, permitting a quantitative assessment of the apparent electron transfer rate constant and how it varies over the heterogeneous surface of AA 2024-T3. These results are important for understanding electrochemical interactions between active coatings (such as conjugated polymer and Mg-rich coatings) and the aluminum alloy. Details are available in the publications cited below.

Archival publications (published) during reporting period by

Bierwagen Group:

Gordon Bierwagen, Kerry Allabar, Brian Hinderliter, Alda M.P. Simões, Dennis Tallman and Stuart Croll, "Ionic Liquid Enhanced Electrochemical Characterization of Organic Coatings," AETOC 2007, accepted in **Progress in Organic Coatings (2008)**,

K. Allahar, B. Hinderliter, A. Simoes, D. Tallman, G. Bierwagen, S. Croll, "Simulation of Wet-Dry Cycling of Organic Coatings using Ionic Liquids," **Journal of the Electrochemical Society** 154 (2007) F177

B. Hinderliter, K. Allahar, G. Bierwagen, D. Tallman and S. Croll, "Using ionic liquids to measure coating properties via electrochemical impedance spectroscopy (EIS)," accepted, **Journal of Coatings Technology & Research**

Tallman Group:

1. B. R. Hinderliter, K. N. Allahar, G. P. Bierwagen, D. E. Tallman, and S. G. Croll, "Thermal Cycling of Epoxy Coatings using Room Temperature Ionic Liquids," **ECS Transactions** 3 (2007) 515-528.
2. M. B. Jensen, T. J. Bjordahl, D. E. Tallman and G. P. Bierwagen "Studies of Electron Transfer at Aluminum Alloy Surfaces by Scanning Electrochemical Microscopy", **ECS Transactions** 3 (31) (2007) 545-555.
3. K. L. Levine, D. E. Tallman and G. P. Bierwagen, "Mott-Schottky Analysis of Aluminium Oxide Formed in the Presence of Different Mediators on the Surface of Aluminium Alloy 2024-T3," **Journal of Materials Processing Technology** 199(1-3) (2008) 321-326.
4. B. R. Hinderliter, K. N. Allahar, G. P. Bierwagen, D. E. Tallman, and S. G. Croll, "Thermal Cycling of Epoxy Coatings using Room Temperature Ionic Liquids," **Journal of the Electrochemical Society** 155 (2008) C93-C100.
5. K. N. Allahar, B. R. Hinderliter, , G. P. Bierwagen, D. E. Tallman, and S. G. Croll, "Cyclic Wet Drying of an Epoxy Coating using an Ionic Liquid," **Progress in Organic Coatings** 62 (2008) 87-95.
6. Mark B. Jensen, Audrey Guerard, Dennis E. Tallman, and Gordon P. Bierwagen, "Studies of Electron Transfer at Aluminum Alloy Surfaces by Scanning Electrochemical Microscopy," **Journal of the Electrochemical Society** 155 (2008) C324-C332.
7. K. N. Allahar, B. R. Hinderliter, D. E. Tallman and G. P. Bierwagen, "Water Transport in Multilayer Organic Coatings," **ECS Transactions** 6(24) (2008) 41-55.
8. Kerry Allahar, Brian Hinderliter, Dennis Tallman and Gordon Bierwagen, "Water Transport in Multilayer Organic Coatings," **Journal of the Electrochemical Society** 155 (2008) F201-F208.
9. D. E. Tallman, "*Dictionary of Electrochemical Science*," Editors: A. J. Bard, G. Inzelt and F. Scholz, entries on buffers (pH, ionic strength, redox), electrode materials (16 types), equilibrium (acid-base, dynamic, electrochemical, redox), frequency (analysis, audio bridge, domain, transformation, dispersion, radio bridge, response analyzer), passivity, transpassivity, resistance (ohmic, solution, uncompensated), noise analysis and flicker noise spectroscopy (2008) in press.
10. Brian R. Hinderliter, Kerry N. Allahar, Gordon P. Bierwagen, Dennis E. Tallman, and Stuart G. Croll, "Water Sorption and Diffusional Properties of a Cured Epoxy Resin Measured using

Alternating Ionic Liquids/ Aqueous Electrolytes in Electrochemical Impedance Spectroscopy,
Journal of Coatings Technology and Research (2008) in press.

Participation at Meetings/Presentations 2008-2009:

The personnel on this project have attended many meetings related to coatings and electrochemistry over this past year, and it is hard to separate specific meetings and presentations that were attended only for this program. However, most of the senior professional staff on this program attended the DoD sponsored Tri-Service Corrosion Conference in Denver, CO in December 2007, and made presentations at this meeting. **As a matter of fact, NDSU had the largest number of presentations at this meeting of any of the academic institutions receiving DOD support.** A list of the presentations that can be specifically tied to this project are given below:

Presentations:

1. "Understanding Reactive Pigments for Cathodic Protection's Impact on Water Transport in Coatings," Brian Hinderliter, Kerry N. Allahar, Stuart Croll, Gordon P. Bierwagen, Dennis E. Tallman and Victoria Gelling, Tri-Service Corrosion Conference 2007, December 3-7, 2007, Denver, Colorado, Oral Presentation.
2. "Water Transport in Air Force Organic Coatings," Kerry N. Allahar, Brian Hinderliter, Dennis E. Tallman, Gordon P. Bierwagen and Stuart Croll, Tri-Service Corrosion Conference 2007, December 3-7, 2007, Denver, Colorado, Oral Presentation.
3. "The Study of Electron Transfer Reactions at AA 2024-T3 by Scanning Electrochemical Microscopy," with Mark B. Jensen, Hosup Jung and Gordon P. Bierwagen, Tri-Service Corrosion Conference 2007, December 3-7, 2007, Denver, Colorado.
4. "Probing Electron Transfer at Complex Interfaces by Scanning Electrochemical Microscopy," Dennis E. Tallman, Audrey Guerard, Mark Jensen and Gordon P. Bierwagen, 3rd International Electromaterials Science Symposium (advanced materials for batteries, energy and solar cells), CSIRO, Clayton, Melbourne, Australia, February 21 – 22, 2008, **Invited Lecture**.

ANNUAL REPORT 2: Reporting Period: September 1, 2008 to August 31, 2009

Change in AFOSR program manager: **Major Michelle Ewy has replaced Maj. Jennifer Gresham as our AFOSR Program Manager**

The objectives of this program remain unchanged from the original statement of work.

Annual accomplishments:

GPBierwagen Group: Work was continued on the use of ionic liquids in emulating cyclic wt-dry exposure using ionic liquids. The acceleration of coating failure using low velocity laminar flow of electrolyte indicates an increase in failure rate without changing the mechanism of failure can be achieved. We are now using embedded electrodes of the type developed in our lab in conjunction with flowing electrolyte to gain further insight to the mechanisms of this type of accelerated failure. The characterization of the cathodic protection of Mg-rich primer for aluminum substrates was continued. The transmission line model was applied to electrochemical impedance spectroscopic data associated with the degradation of a Mg-rich primer. The application of embedded sensors for real time monitoring of Mg-rich primers was performed with the data and analysis reported. The investigation of the AC-DC-AC test protocol for acceleration of coating failure in aircraft coating systems was continued with efforts utilizing embedded sensors demonstrating the applicability of this test method coupled with embedded sensors. New characterization techniques based on Low Angle Microtomy for sample preparation were developed and used in examining exposed samples to determine effects of accelerated aging. Work has been performed on the development of an embeddable reference electrode for use in metal rich coatings to provide continuous monitoring of the OCP of such a system to continuously measure cathodic protection of metal substrates and the change in such coatings on accelerated exposure.

Stuart Croll Group:

Values for the physical properties of coatings are necessary for both the predictive modeling and understanding the connection between accelerated modeling and natural weather exposure. Appearance properties are often dominated by processes occurring at the outer surface and protective properties depend also on the bulk properties. We have found that the natural time dependence of polymer response to any stress lasts longer than the cycle period used in accelerated weathering. Thus mechanical stress does not relax much and builds more in accelerated testing than it does in the diurnal (and longer) cycles of natural conditions. Thus in order to correlate the results of accelerated weathering, we need to factor in higher and different levels of bulk stress and mechanical properties compared to those that would be characteristic of natural weathering.

Photodegradation or mechanical scratches produce surface features in polymers that may relax and diminish after they have been produced. In order to predict, if possible, the connection between accelerated weathering and natural exposure, this relaxation was studied in order to quantify better the damage accumulating in a typical cycle in either environment. Photodegradation-induced roughness and mechanical indentation, near the surface (outer 200 nm) exhibit a significantly lower glass transition

temperature, T_g , than a bulk measurement of T_g . This appears to be genuine and not an artifact of experimental technique or adventitious chemistry. This phenomenon is well known in thermoplastic polymers and now makes the performance of crosslinked coatings more complicated. The practical outcome of this is that the effect of exposure temperature on physical property responses cannot be understood using standard, bulk measurements of glass transition temperature. In addition, when water is absorbed into the coating it softens the polymer again, so water transport and location (as reported last year) makes further differences. Relating laboratory accelerated tests to natural weathering requires that we understand the conditions and effects in both, at a very detailed level.

Dennis E. Tallman Group:

Studies by D. Tallman emphasized the elucidation the role of oxygen in protective coatings performance during their active lifetime of protection. The role of oxygen in the galvanic coupling of poly(pyrrole) and AA 2024-T3 has been fully elucidated and is now published (Yan, Tallman and Bierwagen, 2008).

Studies of electron transfer at AA 2024-T3 using SECM have continued. Using the LabView™ program developed during the previous project period, we have now fit experimentally measured probe approach curves to theory, permitting a quantitative assessment of the apparent electron transfer rate constant and how it varies over the heterogeneous surface of AA 2024-T3 (Jensen et al., manuscript in preparation). These results are important for understanding electrochemical interactions between active coatings (such as conjugated polymer and Mg-rich coatings) and the aluminum alloy. Work was initiated using SECM in combination with scanning electron microscopy and energy dispersive x-ray analysis to study nucleation sites for conjugated polymer electrodeposition on AA 2024-T3. In particular, the role of secondary phase heterogeneities in the nucleation and growth of polymer is being investigated.

Archival publications (studies with at least partial support by this Grant) during reporting period by

Bierwagen Group:

1. Kerry N. Allayar, Vinod Upadhyay, Gordon P. Bierwagen, Victoria Johnston Gelling, “Monitoring of a military vehicle coating under Prohesion exposure by embedded sensors,” **Progress in Organic Coatings**, **65** (2009)142-151
2. Yechun Wang, Gordon P. Bierwagen, “A new acceleration factor for the testing of corrosion protective coatings: flow-induced coating degradation,” **J. Coating Tech Res.** DOI 10.1007/s11998-008-9161-1 (2009)
3. Hong Xu, Dante Battocchi, D.E.Tallman & G.P Bierwagen, “Use of Mg Alloys as Pigments in Mg-Rich Primers for Protection Al Alloys,” **Corrosion** **65** (2009) 318-325,
4. Duhua Wang, Gordon.P Bierwagen, “Sol-gel coatings on metals for corrosion protection, “ **Prog. in Organic Coatings** **64** (2009) 327-338
5. K.N. Allayar, B.R.Hinderliter, G.P. Bierwagen, D.E.Tallman, “Army Vehicle Primer Properties during Wet-Dry Cycling,” **Corrosion** **65** (2009) 126-135

6. Gordon P. Bierwagen, Kerry N. Allahar, Quan Su, Victoria Johnston Gelling, "Electrochemically characterizing the ac-dc-ac accelerated test method using embedded electrodes," **Corrosion Science**, **51** (2009) 95-101
7. Brian Hinderliter, Kerry Allahar, Gordon Bierwagen, Dennis Tallman & Stuart Croll, "Water Sorption and diffusional properties of a cured epoxy resin measured using alternating ionic liquids/aqueous electrolytes in electrochemical impedance spectroscopy," **J. Coating Tech. Research**, **5** (2008) 431-438
8. Kerry Allahar, Quan Su & Gordon Bierwagen, "In Situ Monitoring of Organic Coatings Under QUV/Prohesion Exposure by Embedded Sensors," **Corrosion**, **64** (2008) 860-870
9. Kerry N. Allahar, Quan Su, Gordon P. Bierwagen, Do-Hyung Lee, "Monitoring of the ac-dc-ac Degradation of Organic Coatings using Embedded Electrodes," **Corrosion**, **64** (2008) 773-787
10. K. Allahar, Dante Battocchi, Mark E. Orazem, Gordon P. Bierwagen, Dennis E. Tallman, "Modeling of electrochemical impedance spectroscopic data of a magnesium rich primer," *J. Electrochemical Society*, 155(2008) E143.
11. B. Hinderliter, V. Bonitz, K. Allahar, G. Bierwagen, and S. Croll, "Comparing Transport Properties of Coatings Using High Throughput Methods," Chapter 27, p. 405 in Martin, J.W.; Ryntz, R.A.; Chin, J.; Dickie, R. (Eds.), *Service Life Prediction of Polymeric Materials: Global Perspectives* (ISBN: 978-0-387-84875-4). Springer (NY) Nov. 2008
12. Bret J. Chisholm, Missy Berry, James Bahr, Jie He, Jun Li, Seva Balbyshev, and Gordon P. Bierwagen, "Combinatorial Materials Research Applied to the Development of New Surface Coatings XI: A Workflow for the Development of Hybrid Organic-Inorganic Coatings," **J. Coatings Tech. Res.** (2008)
13. Kerry N. Allahar, Dante Battocchi, Gordon P. Bierwagen, Dennis E. Tallman, "Thermal degradation of a Mg-rich Primer on AA 2024-T3." *ECS Transactions* - San Francisco, CA, Volume 19, "Corrosion (General) - 215th ECS Meeting.
14. Kerry N. Allahar, Duhua Wang, Dante Battocchi, Gordon P. Bierwagen, Séva Balbyshev, "Real time monitoring of an air force topcoat/Mg-rich primer system in B117 exposure by embedded electrodes," reviewed paper in NACE Corrosion/2009, Atlanta, GA., Mar. 2009.
15. Kerry N. Allahar, Quan Su, and Gordon P. Bierwagen, "Non-substrate EIS monitoring of organic coatings with embedded electrodes," submitted to *Progress in Organic Coatings*, 2009.
16. Kerry N. Allahar, Gordon P. Bierwagen, and Victoria Johnston Gelling, "Understanding ac-dc-ac accelerated test results." submitted to the *Corrosion Science*, 2008.
17. K. Allahar, Dante Battocchi, Mark E. Orazem, Gordon P. Bierwagen and Dennis E. Tallman, "Transmission Line Modeling of Electrochemical Impedance Spectroscopic Data of a Magnesium Rich Primer," *Electrochimica Acta* (2009) in press

Tallman Group:

1. M. C. Yan, D. E. Tallman, S. C. Rasmussen, and G. P. Bierwagen, "Corrosion Control Coatings for Aluminum Alloys Based on Neutral and n-Doped Conjugated Polymers," **J. Electrochemical Soc.**, **156** (2009) C360-C366
2. Maocheng Yan, Dennis E. Tallman, Gordon P. Bierwagen, "Role of oxygen in the galvanic interaction between polypyrrole and aluminum alloy," **Electrochimica Acta**, **54** (2008) 220-227
3. M. C. Yan, J. He, D. E. Tallman, S. C. Rasmussen, and G. P. Bierwagen, "Neutral and n-Doped Conjugated Polymers for Corrosion Control of Aluminum Alloys," **ECS Transactions** (2009) in press.
4. M. C. Yan, J. He, D. E. Tallman, S. C. Rasmussen, and G. P. Bierwagen, "Corrosion Control Coatings for Aluminum Alloys Based on Neutral and n-Doped Conjugated Polymers," **Journal of the Electrochemical Society** (2009) in press.

5. J.M. Gustavsson, P.C. Innis, J. He, G.G. Wallace and D.E. Tallman, "Processible Polyaniline-HCSA/poly(Vinyl Acetate-co-Butyl Acrylate) Corrosion Protection Coatings for AA2024-T3: A SVET and Raman study," **Electrochimica Acta** **54**(5) (2009) 1483-1490.

Croll Group: (see above for publications jointly with other Groups on this project)

1. X. Shi, B. R. Hinderliter, S. G. Croll "Environmental and time dependence of moisture transportation in an epoxy coating and its significance for accelerated Weathering" Accepted for publication in **J. Coat. Technol. Res.**, DOI 10.1007/s11998-009-9209-x
2. X. Shi, S. G. Croll, "Thermal-induced recovery of small deformations and degradation defects on epoxy coating surface," Accepted for publication in **J. Coat. Technol. Res.**,
3. Stuart Croll and Brian Hinderliter, "A framework for predicting the service lifetime of composite polymeric coatings," **J. Mater. Sci.**, **43**(20), 6630-6641 (2008) <http://dx.doi.org/10.1007/s10853-008-2645-7>
4. X. Shi, B. M. D. Fernando, S. G. Croll, "Concurrent physical aging and degradation of crosslinked coating systems in accelerated weathering," **J. Coat. Technol. Res.**, **5**(3), 299 - 310 (2008), <http://dx.doi.org/10.1007/s11998-008-9081-0>
5. D. Fernando, X. Shi, S. G. Croll, "Molecular Relaxation Phenomena During Accelerated Weathering of a Polyurethane Coating," **Journal of Coatings Technology and Research**, **5**(1), 1 – 9 (2008) <http://dx.doi.org/10.1007/s11998-007-9077-1>
6. S. G. Croll, X. Shi, B. M. D. Fernando, "The interplay of physical aging and degradation during weathering for two crosslinked coatings," **Progress in Organic Coatings** **61**, 136 – 144 (2008)

Participation at Meetings/Presentations:

The personnel on this project have attended many meetings related to coatings and electrochemistry over this past year, and it is hard to separate specific meetings and presentations that were attended only for this program. However, many of the senior professional staff on this program attended the DoD Corrosion Conference in Washington DC in August 2009, and made presentations at this meeting. A list of the presentations that can be specifically tied to this project are given below:

Presentations: (First person in author list or underlined author were presenters)

1. Gordon Bierwagen, Roger Brown, Dante Battocchi and Scott Hayes, "Observations on the testing of Mg-rich Primers for Totally Chromate – free Corrosion Protection of Aerospace Alloys", DOD Corrosion Conference 2009, Aug. 10-14, 2009, Washington, DC, Oral Presentation by GPB and R. Brown. Written manuscript in Conf. Proceedings on CD.
2. Kerry N. Allabar and Gordon P. Bierwagen, "Characterizing the relaxation potential of an ac-dc-ac accelerated test," Oral Presentation by KNA. Written manuscript in Conf. Proceedings on CD, DOD Corrosion Conference 2009, Aug 10-14, 2009 Washington D.C.,
3. Kerry N. Allabar, Dante Battocchi and Gordon P. Bierwagen, "Electrochemical noise monitoring of the cathodic protection of Mg-rich primers," Oral Presentation by KNA. Written manuscript in Conf. Proceedings on CD, DOD Corrosion Conference 2009, Aug 10-14, 2009 Washington D.C
4. Gordon Bierwagen, "Active Metal-Based Corrosion Protective Coating Systems for Aircraft Requiring No Chromate Pretreatment," Presented at Coating Science International (CoSI) 2009, Noordwijk, The Netherlands, June 24, 2009

5. Xiaodong Shi, Brian R. Hinderliter, Stuart G. Croll, "The effect of moisture transport on corrosion protective coatings, or, being careful with accelerated weathering," Army Corrosion Summit, Clearwater, FL, Feb 3-5, 2009
6. X. Shi, B. R. Hinderliter, S. G. Croll, "The Role of Moisture Transportation in Varying the Effect of Accelerated Weathering," Coatings Tech 2009 Indianapolis, April 28 – 29, 2009.
7. Xiaodong Shi, Stuart G. Croll, "Recovery of Small Deformation and Degradation Defects on an Epoxy Coating Surface," FutureCoat 2008, Chicago 15-16th October.
8. Kerry N. Allahar, Duhua Wang, Dante Battocchi, Gordon P. Bierwagen, Séva Balbyshev, "Real time monitoring of an air force topcoat/mg-rich primer system in B117 exposure by embedded electrodes," NACE Corrosion/2009, Atlanta, GA.
9. Kerry Allahar, Duhua Wang, Dante Battocchi, Gordon Bierwagen, "Electrochemically detecting defects in an Air Force topcoat/Mg-rich primer system with embedded electrodes." Research in Progress Session 1, NACE Corrosion/2009, Atlanta, GA.
10. Kerry N. Allahar, Dante Battocchi, Gordon P. Bierwagen, Dennis E. Tallman, "Thermal degradation of a Mg-rich Primer on AA 2024-T3." 215th Electrochemical Society Meeting, San Francisco, May 2009.
11. Kerry N. Allahar, Dante Battocchi, Gordon P. Bierwagen, Séva Balbyshev, "Cathodic protection of AA 2024-T3 by a Mg-rich primer," 17th International Corrosion Congress, Las Vegas, Nevada, Oct. 2008.
12. Kerry N. Allahar, Gordon P. Bierwagen, and Victoria Johnston Gelling, "Understanding ac-dc-ac accelerated test results," EuroCorr 2008, The European Corrosion Congress, Edinburgh, UK, Sept. 2008.
13. Kerry N. Allahar, Quan Su, and Gordon P. Bierwagen, "Embedded electrodes for EIS monitoring of organic coatings without the substrate as an electrode," EuroCorr 2008, The European Corrosion Congress, Edinburgh, UK, Sept. 2008.
14. Y. Wang and G. P. Bierwagen, "A new acceleration factor for differentiating marine coatings: flow-induced coating degradation", International Marine & Offshore Coatings Conference, Virginia Beach, VA, May 18-20, 2009.
15. Y. Wang and G. P. Bierwagen, "Flow-induced degradation of corrosion protective coatings: A new acceleration factor for testing", AIChE 2009 Annual Meeting, **Nashville, TN**, Nov. 2009.
16. Maocheng Yan, Jie He, Dennis E. Tallman, Seth C. Rasmussen, and Gordon P. Bierwagen, "Neutral and n-Doped Conjugated Polymers for Corrosion Control of Aluminum Alloys," *214th ECS Meeting, 2008 Fall Meeting of The Electrochemical Society of Japan, October 12-17, 2008, Honolulu, HI, Oral Presentation.*
17. Dennis E. Tallman, "Probing the Intricacies of Corrosion," *ACES: Electromaterials Symposium 2009 "Nanostructured Electromaterials,"* February 4-6, 2009, University of Wollongong, Wollongong, Australia, **Invited Speaker.**
18. Dennis . E. Tallman, Maocheng Yan, Seth C. Rasmussen and Gordon P. Bierwagen, "Neutral and n-Doped Conjugated Polymers for Corrosion Control of Aluminum Alloys," Fourth International Conference on Advanced Materials and Nanotechnology (AMN-4), February 8-12, 2009, the University of Otago, Dunedin, New Zealand, **Invited Speaker.**
19. B. Merten, D. Battocchi, D. Tallman and G. Bierwagen, "Embedded Reference Electrode for Potential-Monitoring of Cathodic Protective Systems," *215th ECS Meeting, May 24-29, 2009, San Francisco, CA, Oral Presentation.*

For the work period Sept. 2009 to June 30, 2010, the termination of the contract, the following archival publications resulted, all or in part, from this grant:

Bierwagen Group

K. Allahar; Dante Battocchi, Gordon P Bierwagen, Dennis E Tallman, “Thermal degradation of a Mg-Rich primer on AA 2024-T3,” submitted to **Corrosion Science** March 2010

Kerry N. Allahar, Vinod Upadhyay, Gordon P. Bierwagen, “Characterizing the relaxation of the open circuit potential during an ac-dc-ac accelerated test,” **CORROSION** **66** (2010) 095001

Kerry N. Allahar, Quan Su, Gordon P. Bierwagen, “Electrochemical noise monitoring of the cathodic protection of Mg-rich primers,” **Corrosion** **66** (2010) 085003 1-13

K.N. Allahar, D. Wang, D.Battocchi, G.P.Bierwagen & S. Balbyshev, “Real-time Monitoring of a US Air Force Topcoat/Mg-Rich primer System in ASTM B117 Exposure,” **Corrosion** **66** (2010) 075003-1 to 075003-11

Neena Ravindran, Dipak K. Chatterpadhyay, Autumn Zakula, Dante Battocchi, Dean C. Webster & Gordon P. Bierwagen, “Thermal Stability of Mg-rich Primers based on Glycidyl Carbamate Resins,” **Polymer Degradation & Stability** **XXX** (2010) 1-7

Maocheng Yan, Victoria J. Gelling, Brian R. Hinderliter, Dante Battocchi, Dennis E. Tallman, Gordon P. Bierwagen, “SVET method for characterizing anti-corrosion performance of metal-rich coatings,” **Corrosion Science**, **XX** (2010) **XXX**

Gordon Bierwagen, Andrew Huovinen, and Bobbi Jo Merten, “Surface Energetics,” Ch. 37 in *ASTM Paint and Coating Testing Manual*—17th Edition, to be published in 2010

Quan Su, Kerry N. Allahar, Gordon P. Bierwagen, “In-situ embedded sensor monitoring of an Air Force primer beneath a topcoat exposed to atmospheric humidity and thermal conditions,” **CORROSION**, **66** (2010) 066001

Gordon Bierwagen and Andrew Huovinen, VOL 4 Control of Corrosion by Surface Treatment and Coatings: “Paint Formulation” Ch. 143, pp 2643-2665 of *Shreirs CORROSION 4th Edition*, Elsevier (Amsterdam) 2010 6 Volume Reference Book

B. E.Merten, D.Battocchi, D. E. Tallman and G. P. Bierwagen, “Embedded reference electrode for potential-monitoring of cathodic protective systems,” **ECS Transactions** **19**(29) (2009) 223-232.from Corrosion (General)--215th ECS Meeting, 2009

Kerry.Allahar, Gordon Bierwagen Dante Battocchi and Dennis Tallman, “Transmission Line Modeling of EIS Data for a Mg-Rich Primer on AA 2024-T3,” **J. Electrochem. Soc** **153** (2010) C95-C101

Kerry N. Allahar, Josiah Bjorgaard, Gordon P. Bierwagen, “Mg-Rich primer performance under mechanical strain,” (accepted for *ECS Transactions on Organic Coatings for Corrosion Control V* Cambridge Sept.2009)

Jinhai Wang, Gordon Bierwagen, Hong Xu, and Dante Bottocchi, "On the oxidation products in Mg-rich primers: I. the case of pure Mg pigment," in *Fifth International Symposium on Advances in Corrosion Protection by Organic Coatings* **ECS Transactions 24(1)** (2010) 247-259 The Electrochemical Society, Pennington, NJ

J. Nie, M. C. Yan, J. Wang, D. E. Tallman, D. Battocchi, G. P. Bierwagen, "Cathodic Corrosion Protection Performance of Mg-Rich Primers: Effect of Pigment Shape and Pigment Volume Concentration," in *Fifth International Symposium on Advances in Corrosion Protection by Organic Coatings* **ECS Transactions 24(1)** (2010) 261-275 The Electrochemical Society, Pennington, NJ

Kerry N. Allahar, Gordon P. Bierwagen, Victoria Johnston Gelling, "Understanding ac-dc-ac accelerated test results," **Corrosion Science**, **52** (2009) 1106-1114

Kerry Allahar, Quan Su, Gordon Bierwagen, "Non-substrate EIS monitoring of organic coatings with embedded electrodes," **Prog. Organic Coatings**, **67** (2010) 180-187

Gordon Bierwagen, Roger Brown, Dante Battocchi, Scott Hayes, "Active metal-based corrosion protective coating systems for aircraft requiring no chromate pretreatment," **Prog. Organic Coatings**, **67** (2010) 195-208

Duhua Wang, Dante Battocchi*, Kerry N. Allahar, Seva Balbyshev, Gordon P. Bierwagen, "In situ monitoring of a Mg-rich primer beneath a topcoat exposed to Prohesion conditions," **Corrosion Science** **52** (2010) 441-448

M. C. Yan, D. E. Tallman, S. C. Rasmussen, and G. P. Bierwagen, "Corrosion Control Coatings for Aluminum Alloys Based on Neutral and n-Doped Conjugated Polymers," **J. Electrochemical Soc.**, **156** (2009) C360-C366

Yechun Wang, Gordon P. Bierwagen, "A new acceleration factor for the testing of corrosion protective coatings: flow-induced coating degradation," **J. Coating Tech Res.** **6** (2009) 429-436

Hong Xu, Dante Battocchi, D.E.Tallman & G.P Bierwagen, "Use of Mg Alloys as Pigments in Mg-Rich Primers for Protection Al Alloys," **Corrosion** **65** (2009) 318-325

B. R. Hinderliter, S. G. Croll, "Predicting Coating Failure using the Central Limit Theorem and Physical Modelling," ECS Transactions Volume: 24(1), 1- 26 (2010) (Fifth International Symposium on Corrosion Protection by Organic Coatings, September 14 - September 18, 2009 , Cambridge, UK, Proceedings Editor(s): M. Kendig, D. Scantlebury

X. Shi, S.G. Croll, "Recovery of surface defects on epoxy coatings and implications for the use of accelerated weathering," *Prog. Org. Coat.*, 68(1-2) , 79 - 87 (2010) [doi:10.1016/j.porgcoat.2009.08.019](https://doi.org/10.1016/j.porgcoat.2009.08.019)

X. Shi, B. R. Hinderliter, S. G. Croll “Environmental and time dependence of moisture transportation in an epoxy coating and its significance for accelerated weathering” J. Coat. Technol. Res., 7(4) 419 -430 (2010) <http://dx.doi:10.1007/s11998-009-9209-x>

X. Shi, S. G. Croll, “Thermal-induced recovery of small deformations and degradation defects on epoxy coating surface,” J. Coat. Technol. Res., 7 (1), 73 – 84, 2010 <http://dx.doi 10.1007/s11998-009-9176-2>

S. G. Croll, “Application of the Flory-Rehner Equation and the Griffith Fracture Criterion to Paint Stripping,” J. Coat. Technol. Res., 7 (1), 49 – 55, 2010 <http://dx.doi 10.1007/s11998-009-9166-4>

The following Presentations of results generated, all or in part, from this grant in the time frame Sept 2009 to June 30, 2010, are as follows:

Gordon Bierwagen & Tiantian Chen, “Studies of Flexible Mg-rich (Chromate-free) Primers for Aircraft,” NACE Eastern Area Conference 2010, Alexandria, VA, USA, to be presented October 12-15, 2010

Gordon Bierwagen, “Mg-Rich Chromate Free Primers for Aircraft,” Plenary Lecturer for PaintIstanbul Congress., Turkish Paint Industry Association (BOSAD) presented September 23-26, 2010

Gordon P. Bierwagen,^{a*} Kerry N. Allahar^a, Vinod Upadhyay^a “Extracting New Information from Enhanced AC-DC-AC Accelerated Testing of Coated Metals,” EIS 2010 June 6 - 11, 2010 • Hotel Tivoli Carvoeiro • Carvoeiro, Algarve, Portugal

Gordon Bierwagen and Dante Battocchi,” Mg-rich Primers for Aluminum Alloys – Gaining Acceptance of a New Paradigm is not Easy”, presented at *Advances in Corrosion Protection by Organic Coatings V*, Cambridge, UK Sept.19, 2009

Kerry N. Allahar, Josiah Bjorgaard, Gordon P. Bierwagen, “Mg-Rich primer performance under mechanical strain,” presented at *Advances in Corrosion Protection by Organic Coatings V*, Cambridge, UK Sept.19, 2009

Kerry N. Allahar*, Dante Battocchi, Gordon P. Bierwagen, Dennis E. Tallman, Thermal degradation of a Mg-Rich primer on AA 2024-T3,” presented at 215th Electrochemical Society Meeting, San Francisco, CA Sept. 2009

B. R. Hinderliter and S. G. Croll*, “Predicting Coating Failure using the Central Limit Theorem and Physical Modelling,” *Corrosion Protection by Organic Coatings*, Christ's College, Cambridge, 14-18 September 2009

S. G. Croll, “ I. Predicting Coating Durability; II. Problems correlating Accelerated Exposure to Real Life,” Asian Paints, Navi Mumbai, October 12th, 2009

S. G. Croll, “ I. Predicting Coating Durability; II. Problems correlating Accelerated Exposure to Real Life,” invited talk at Eastman Chemicals, Kingsport TN, 3rd December, 2009

S. G. Croll, B. R. Hinderliter, “Multiphysics models for the deterioration of corrosion protection by barrier coatings,” Coatings Science International, Noordwijk, The Netherlands June-July 2010

A Program Review Meeting in Alexandria VA for the AFOSR 2009 Surface and Interfacial Science Portfolio took place Oct. 13, 2009. For this grant the following information was presented:

**AFOSR Program Review
for Grant FA9550-07-1-0370:
Characterization, Modeling, and
Accelerating Emulation of Aircraft
Coating Exposure and Degradation**

**Prof. Gordon Bierwagen, PI
Dept. of Coatings & Polymeric Materials
North Dakota State University**

AFOSR Review 13 Jan 2009

Outline of Presentation



I. Brief Discussion of Work Through 2009

II. Work of NDSU Group in 2009

- A. Room Temperature Ionic Liquid Studies
- B. CPVC Studies
- C. Characterization Studies
 - 1. Low Angle Microtome Methods
 - 2. Fluorescence Microscopy
- D. Flow Induced Degradation Studies

**III. General Issues on Accelerated Testing and
Lifetime Prediction of Aircraft Coatings**

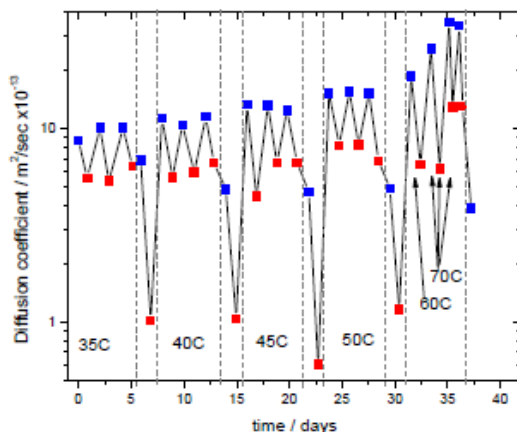
Research Activities for AFOSR



Current

- Mg rich primer
 - Experiments conducted with temperature as a variable to determine consistency of modeling parameters with Arrhenius behavior
- Monitoring Mg-rich primer/topcoat with embedded sensors
 - Experiments conducted with scribed panel to determine the influence of defects on the EIS and ENM parameters
- Modeling of scaled OCP relaxation associated with Air Force coatings
 - Experiments conducted with temperature as a variable to determine consistency of the modeling parameters with Arrhenius behavior
- Dynamic Bend testing of Air Force coatings under accelerated conditions
- Influence of atmospheric conditions and UV light exposure on the degradation of corrosion barrier protection of Air Force coatings

Diffusion Coefficient derived from Fitting of EIS at 10^4 Hz



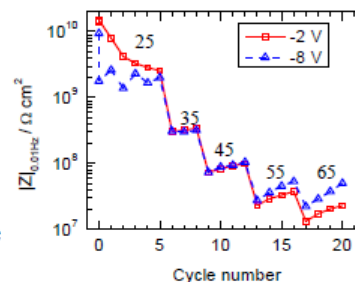
- 3 replicates at each temperature are consistent
- Diffusion coefficient with water ingress is higher than water egress (RTIL as electrolyte)
- Room temperature diffusion coefficients return to initial values

What have we learned thus far in Coatings with new RTIL's

- RTIL's allow characterization of coatings in drying unavailable in aqueous electrolytes
- Continuous system monitoring at single frequency (greater than system response time) in EIS gives dynamic picture of processes occurring in coating exposure and field use
- Data from System now available:
 - Local Conductivity, Capacitance of Coating during drying as well as drying cycles, Volume fraction of water vs time in coatings, insight into effects of conductive pathways in coatings, Diffusion coefficients for water in wetting as well as drying
- In conjunction with measurement techniques, they offer new insight into dielectric effects in coatings, especially transport effects

Thermal influence on ac-dc-ac accelerated testing

- ac-dc-ac cycles
 - a.c. step: EIS (ENM)
 - cathodic potential d.c. step
 - rest period: relaxation of OCP
- Barrier property was consistent with Arrhenius behavior
- Modeled scaled E_{OC} relaxation profile with 3 characteristic time model
 - Characteristic times
 - diffusion (10^4 s) > dielectric relaxation (10^3 s) > charge transfer (10^2 s)
 - Pre-exponential parameters consistent with Arrhenius behavior in 35 °C to 55 °C range

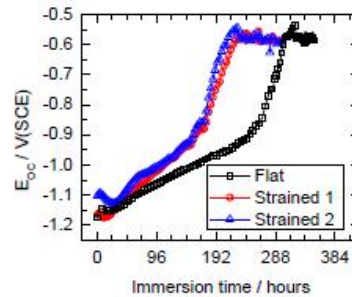


Influence of mechanical strain on Mg-rich primer performance

- Similarity between flat and strained panels during CP loss

- Barrier property
- Dielectric property at 10 kHz

- 6% strain yielded 27% loss in CP



- Transmission line model fit data

- Similarity between flat and strained parameters as functions of E_{oc} support the observation that the mechanism of CP loss/ Mg degradation was similar for both flat and strained panels

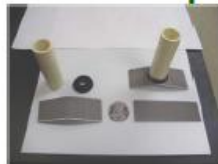
- Parameter R_1 had a faster change with time indicating that the faster loss of CP was due to the interfacial processes

NDSU

Department of Coatings
and Polymeric Materials

- Strain caused defects by Mg particles thereby increasing surface area

Dynamic Exposure Chamber Samples and Side View



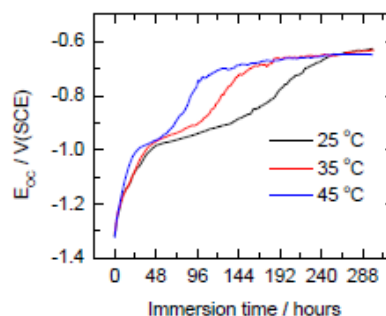
NDSU

Department of Coatings
and Polymeric Materials

AFOSR Review 13 Jan 2009

Thermal influence on Mg-rich primers

- Transient profiles for E_{OC}
 - Distinguishable stages
 - Similar for different temperatures
- Cathodic protection (CP) loss
 - faster at higher temperatures
 - increases in $|Z|_{0.01\text{Hz}}$ and $C_{10\text{kHz}}$
- Transmission line modeling
 - Fit for range 0.01 Hz to 1 kHz
 - Loss in CP associated with changes in interfacial resistance parameter
- Arrhenius plot of parameters
 - Opposite signs for R_e and R_i supports model



NDSU Department of Coatings and Polymeric Materials

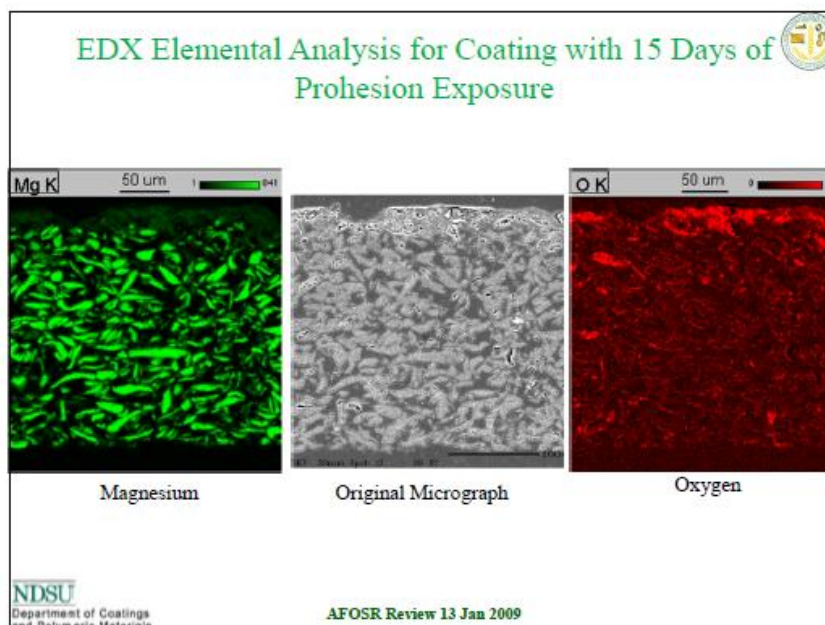
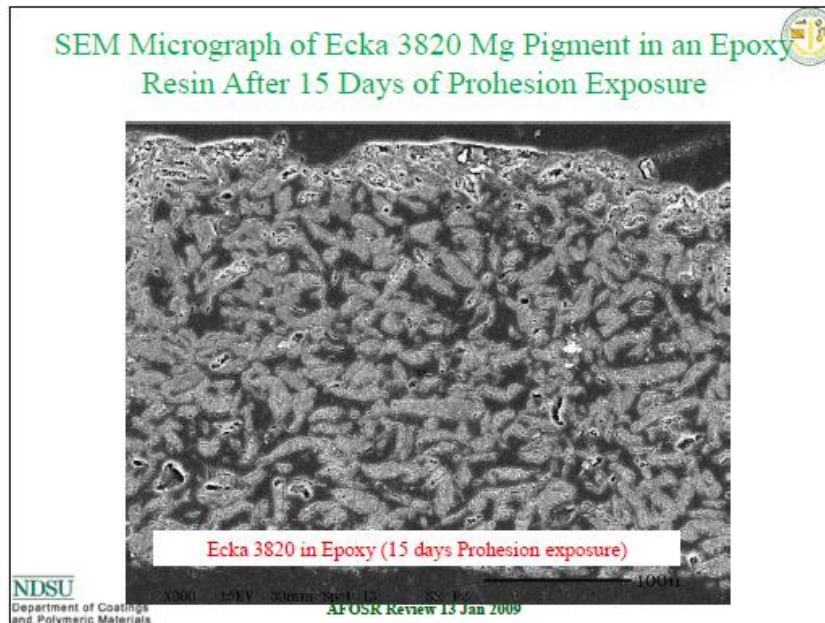
• Increase in E_A for conductivity with loss in CP supports model

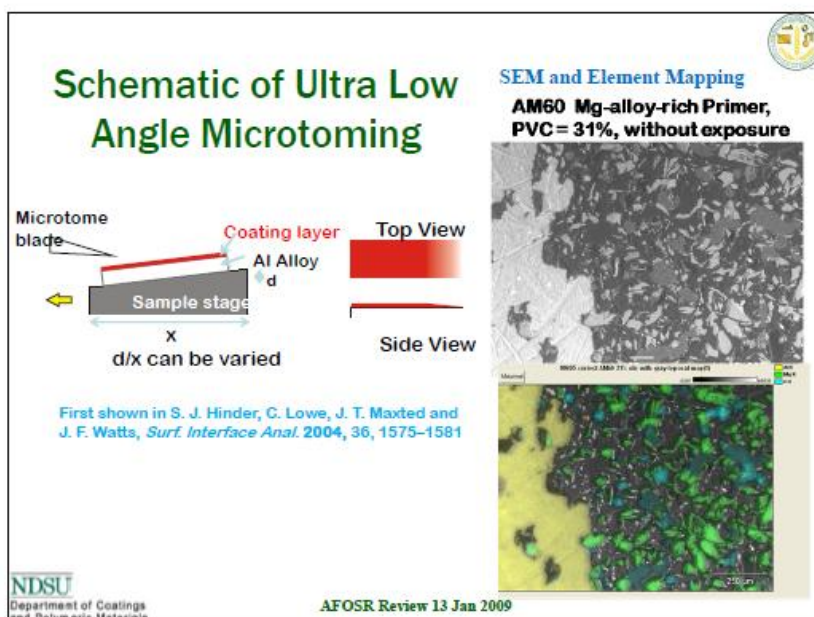
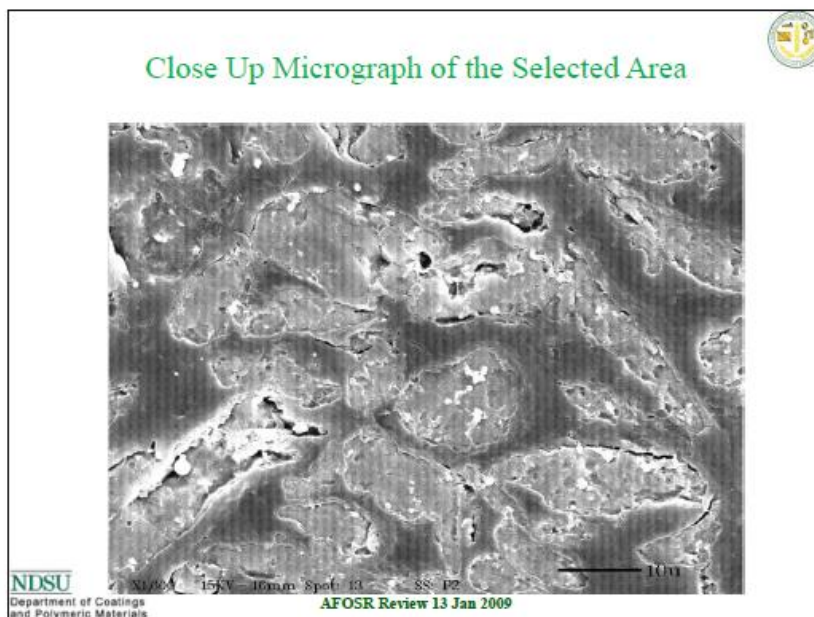
Pigment Volume Fraction and Particle Packing Effects in Coating Design and Performance

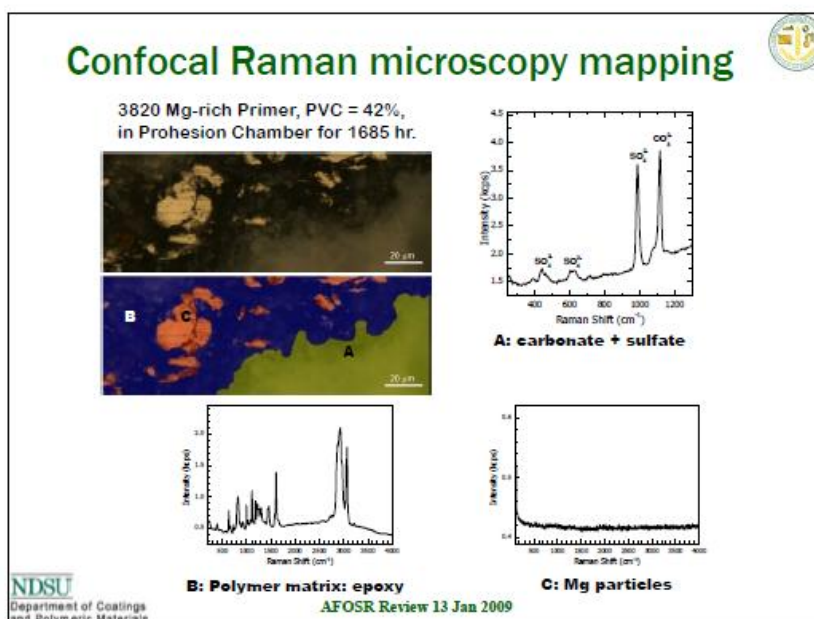
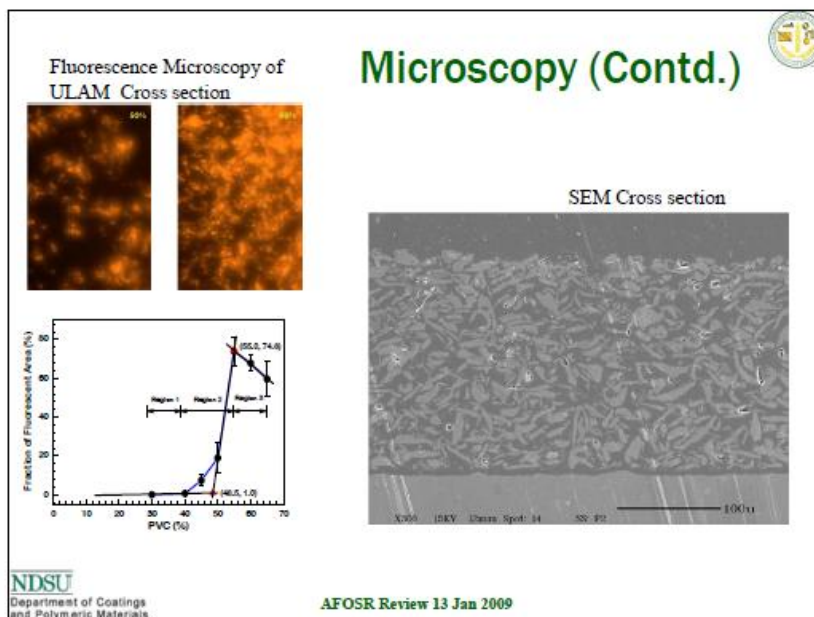
- Modeling "Coarseness" of pigment-polymer distribution + allowing voids gives realistic predictions of film behavior.
- Calculations & model yield qualitative agreement with real systems.
- Hard Sphere/Monte Carlo Packing Modeling gives extraordinary insight into particle packing in coatings films
- Work ongoing to include percolation analyses into coating modeling
- We are continuing studies of Packing efficiencies in our work (discussed below) on metal-rich primer coatings. We are examining shape and orientation effects in particle packing as well as connectivity of particles in corrosion protection.
- Future work will model particle packing, flocculation, etc. and test results quantitatively with experimental film properties.
- Further work needs to be done to account for particle size distribution effects

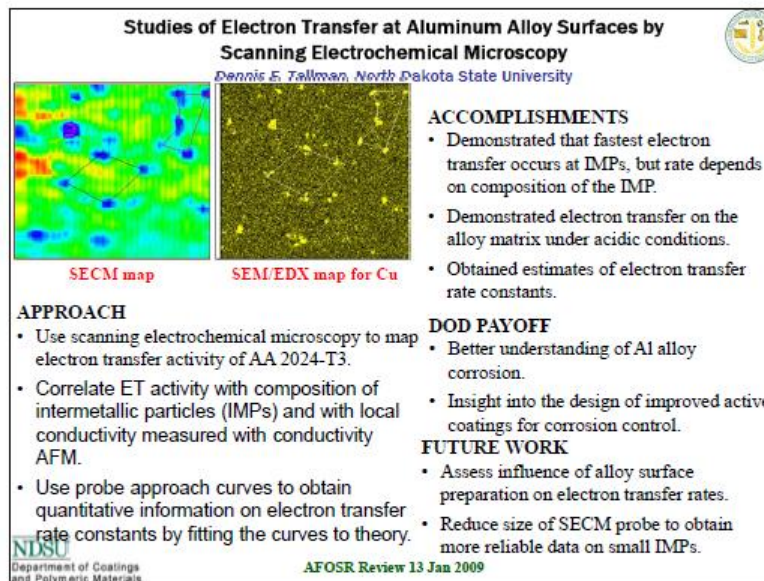
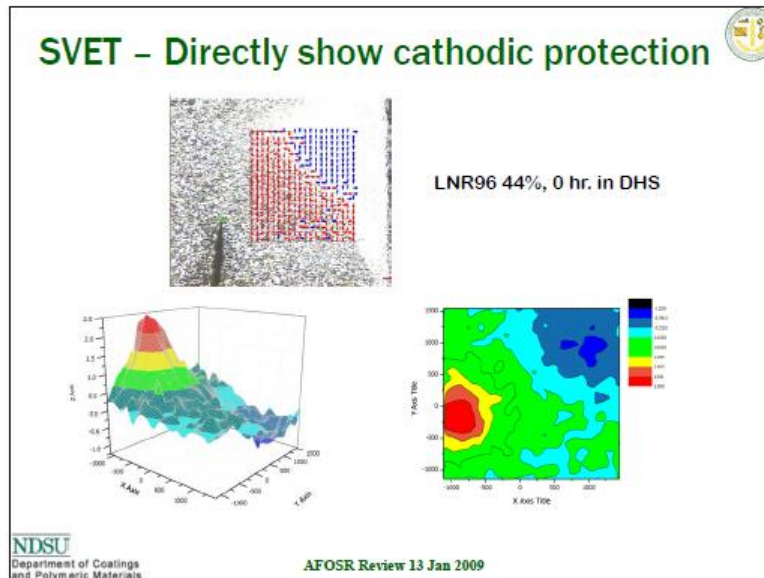
NDSU Department of Coatings and Polymeric Materials

AFOSR Review 13 Jan 2009







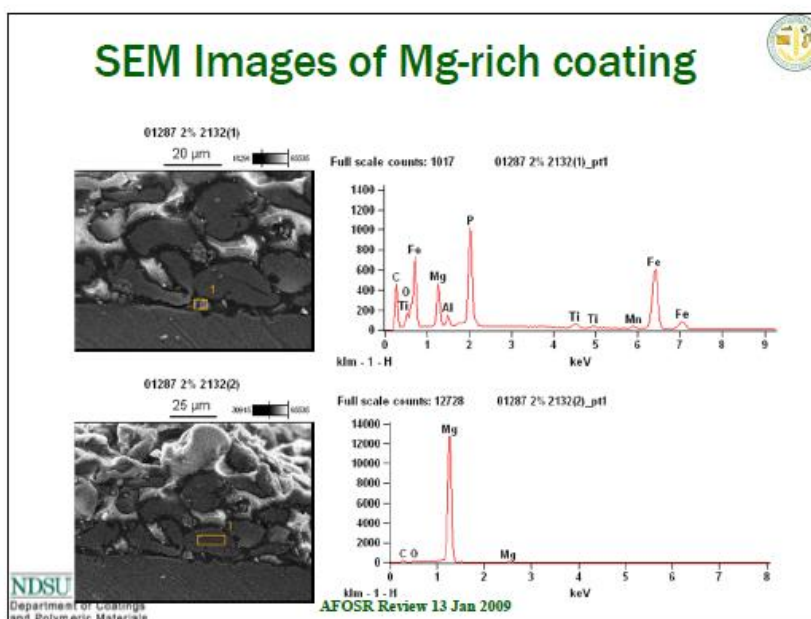
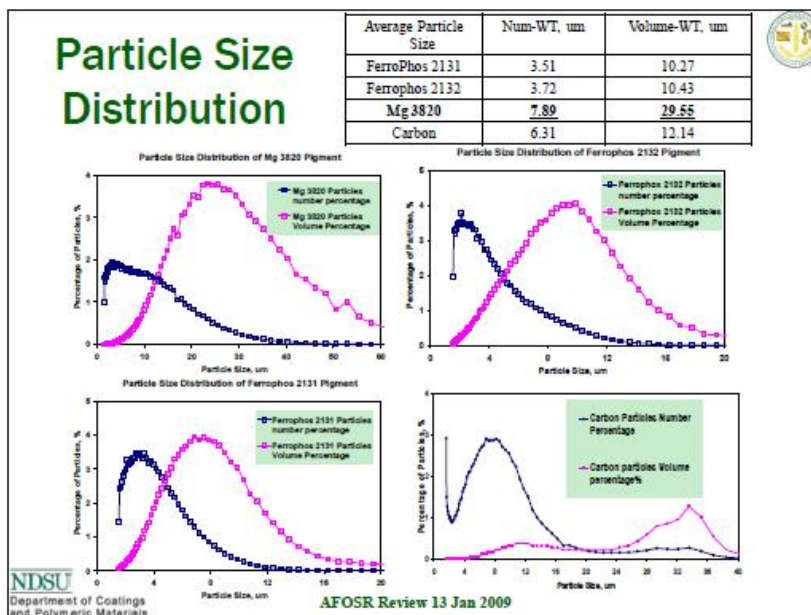


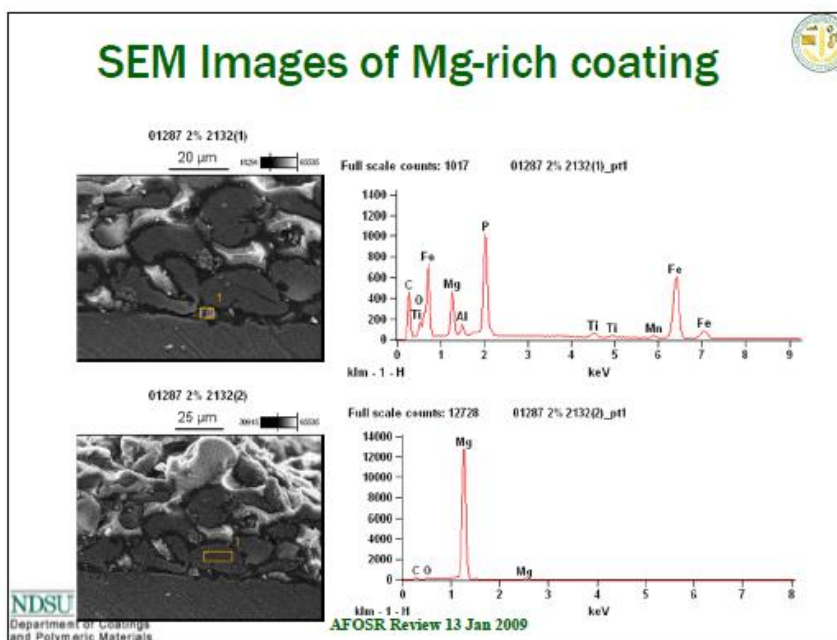
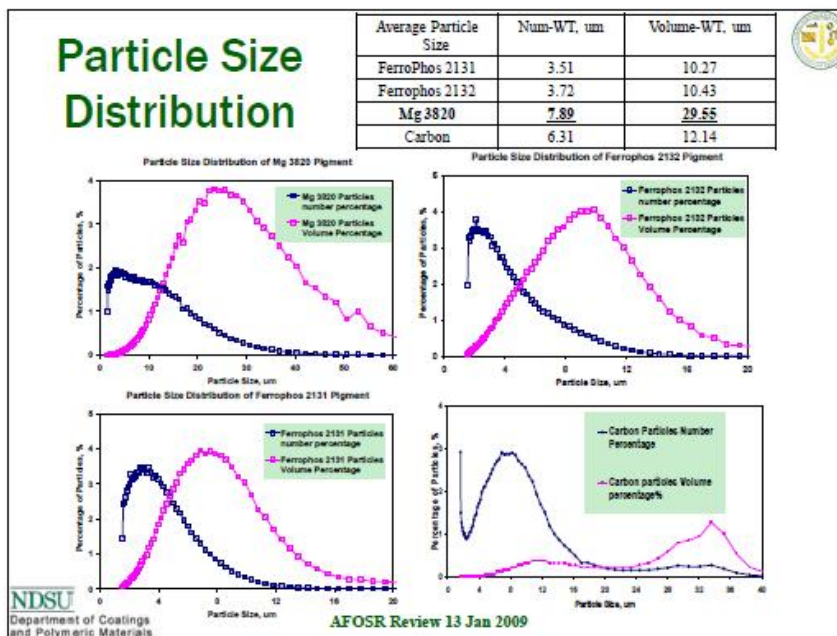
New Recent Issues

- Work of Prof. Tallman's group implies O₂ Sequestration/ Scavenging by active materials, including Mg particles in Mg-rich primers, may explain some of the corrosion protective function of active coatings
- In the case of the Mg-rich systems, the O₂ Scavenging effects may possibly be interpreted by Cussler's analysis of chemically active species in a film
- The lag time τ for a diffusing material such as O₂ without scavenging is $\tau = l^2/6D$, where l is the film thickness and D is the diffusion coefficient. When there is scavenging of the diffusing material, in our case O₂, the lag time is $\tau = l^2/6D(1 + 3C_{scav}/vHC_{O_2})$ where v is the stoichiometric coefficient for the scavenging of O₂.

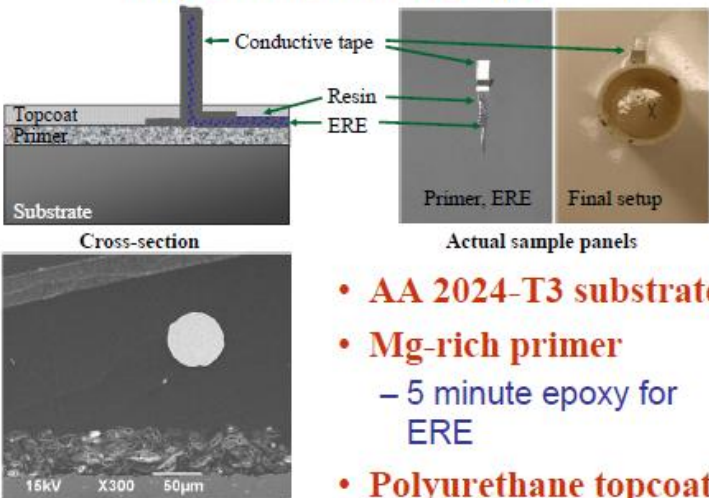
Recent Issues

- We are beginning studies to exam the effects of this scavenging on the later stages of Mg-rich coating lifetime. Current results indicate corrosion protection by the MgR systems even when there is no longer cathodic protection. This scavenging effect may contribute to the extra-ordinary (MgR primer + topcoat) that has been observed within the AF and other military services.





Experimental Setup



Cross-section

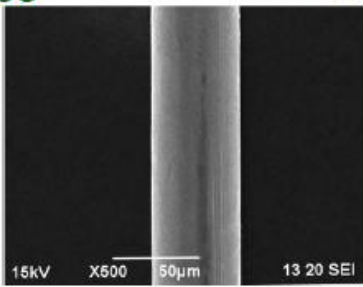
Actual sample panels

- **AA 2024-T3 substrate**
- **Mg-rich primer**
 - 5 minute epoxy for ERE
- **Polyurethane topcoat**

NDSU
Department of Coatings and Polymeric Materials

AFOSR Review 13 Jan 2009

Objectives



- A. Fabricate and embed Ag/AgCl reference electrodes**
 - Adhere wire electrode between primer and topcoat
 - Lead to external equipment must be secure
- B. Obtain OCP measurements using the ERE**
 - Constant immersion testing
 - Apply potential and monitor response
- C. Investigate in-situ performance via B117 salt spray**
 - OCP and Electrochemical impedance spectroscopy (EIS)

Silver (Ag) wires
50 µm diameter
Chemically oxidized
0.03M FeCl₃
60 seconds

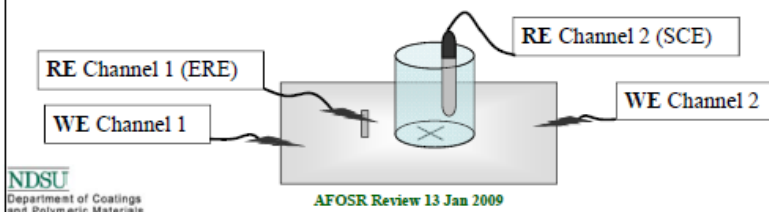
AgCl layer deposits
Stable Ag/AgCl mixed potential is established

NDSU
Department of Coatings and Polymeric Materials

AFOSR Review 13 Jan 2009

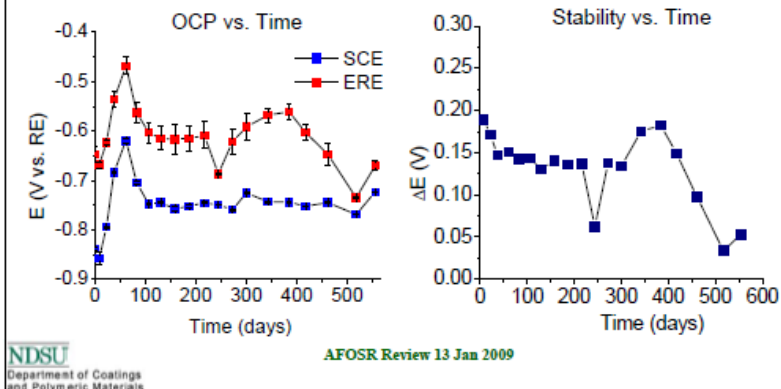
Experimental Methods – I. OCP

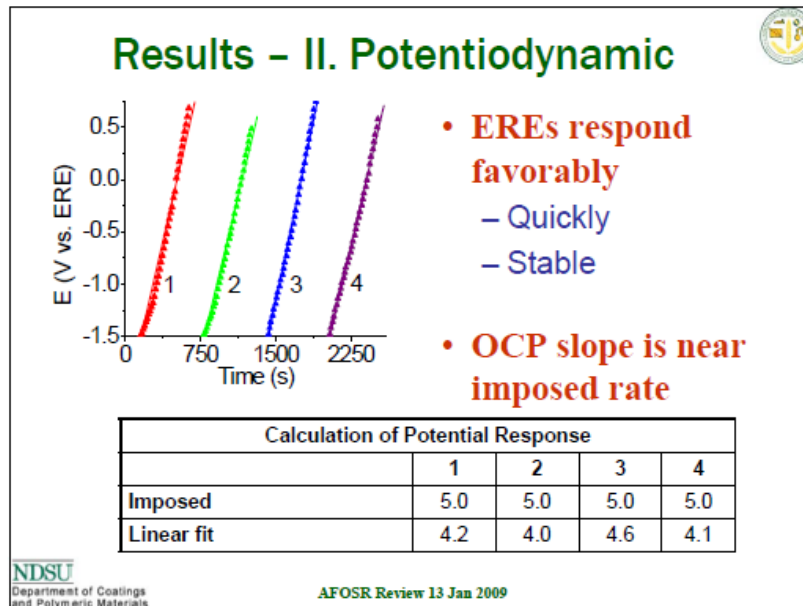
- **Multiplexed potentiostat**
 - OCP vs. ERE, OCP vs. saturated calomel electrode (SCE)
 - Near-simultaneous measurements
- **ΔE should not change over time**
- **E vs. ERE expected to be -300 mV to -900 mV**



Results – I. OCP

- **E vs. ERE is approximately -600 mV**
 - Ranges from 25 to 175 mV more positive than E_{SCE}





II. Fracture Strength

Crucial to many properties, inc. corrosion

Griffith's criterion for stress at fracture (toughness) in brittle materials:

$$Stress_G = \sqrt{\frac{2EG}{\pi a}} = Stress_{External} + Stress_{Internal}$$

Assuming the largest initiating crack (pit) is n standard deviations deep (using zero order kinetics):

$$Stress_G = \sqrt{\frac{2EG}{\pi n \sqrt{\sigma_{initial}^2 + kt}}}$$

Simplifying and scaling to initial fracture stress gives:

$$\frac{Stress_G(t)}{Stress_G(t=0)} = (1 + kt / \sigma_{initial}^2)^{-1/4}$$

- Possible linkage between gloss and toughness via ' k ' and $\sigma_{initial}$.

NDSU
Department of Coatings and Polymeric Materials

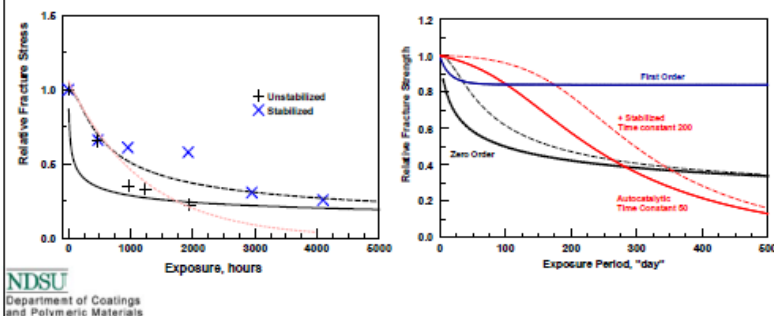
30

Application to Fracture Strength

Data from: M.E. Nichols, C.A. Peters, 'The effect of weathering on the fracture energy of hardcoat over polycarbonate', Polym. Degrad. Stab., 75 (2002) 439-446 (permission from M.E. Nichols)

The line is a fit (zero order) obtained from raising the relative fracture strength to 4th power.
Plausible fit, but too few data to be conclusive.

If there were more data points, we could have justified some of the options below.



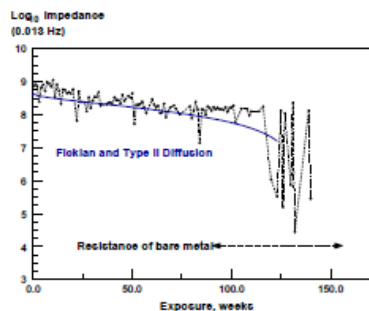
NDSU
Department of Coatings
and Polymeric Materials

31

Corrosion Protection

Model of Electrochemical Impedance Spectroscopy

- If water gets in via Diffusion ($t^{1/2}$) and linear t , damage process (Case II Diffusion?)
 - Then the resistance (low frequency impedance) of the coating will diminish as the water shorts out that depth (data from Gordon Bierwagen)
- Thickness of the film, d , is reduced by: $d(t) = d_0 - (D_H t + \sqrt{D_F t})$
- We can calculate the impedance of the film, assuming a parallel RC equivalent.
- Coating life is limited at downturn
- Failure is when water arrives at substrate
 - vs. size of thin spot, plugging



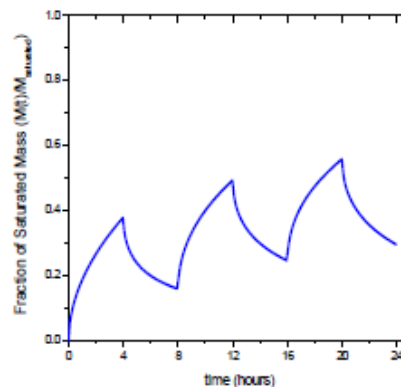
- N.B. Percolating water channels seem to follow a log-normal arrival time distribution (Monte Carlo calculation)
- D 's to left will be scaled by the exposure cycle period

NDSU
Department of Coatings
and Polymeric Materials

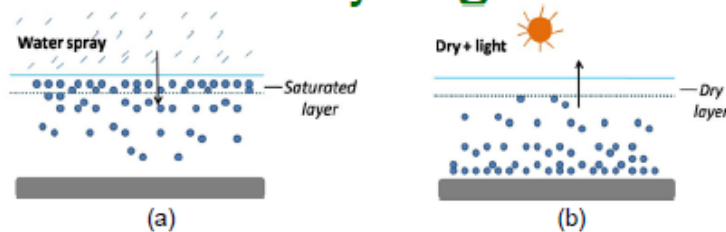
32

Total Water Uptake in Cyclic Exposures

- The total water mass in the coating increases at the end of each wet cycle.
- The dry cycle removes some water, but not all.
- Depends on time and temperature
- The cycles are not yet equivalent here



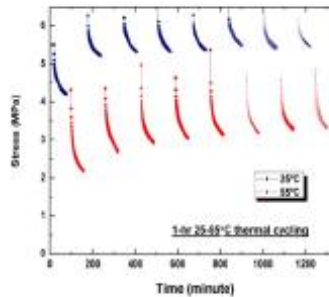
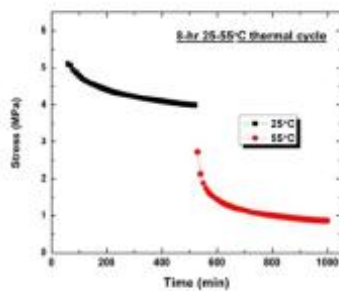
Possible water transport with cycling



Schematic illustration of water molecule distributions. Differences may occur depending on whether there is time for the whole coating to saturate or to dry.

- Depending on where the water is, and whether the material T_g is affected
 - the rate of degradation chemistry may be altered
 - the rate of any physical change may be altered
 - failure mechanism may be different, e.g. adhesive vs. cohesive

Time – Dependence example: Stress relaxation in cycles



- Equivalent length of experimental time at both temperatures;
- Stress built up in the short cycles; much less in long cycles
 - Short cycles may cause failures but long cycles may never
- How about moisture?